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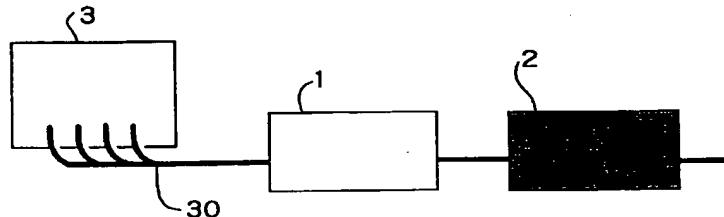
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(54) Apparatus for purifying exhaust gas emitted from diesel engine

(57) An apparatus for purifying an exhaust gas emitted from a diesel engine (3) includes an oxidizing catalyst (1), and a sulfate-storing-and-reducing catalyst (2). The oxidizing catalyst is disposed on an upstream side in an exhaust system (30) of a diesel engine, and can oxidize at least HC (i.e., hydrocarbons) contained in an exhaust gas emitted from the diesel engine. The sulfate-storing-and-reducing catalyst can not only capture precursors of sulfates (i.e., SO₃, SO₄²⁻, H₂SO₄, etc.), generated at the oxidizing catalyst, as sulfates, but also can

reduce the captured sulfates to SO₂, and is disposed on a downstream side with respect to the oxidizing catalyst in the exhaust system. The sulfate-storing-and-reducing catalyst turns the precursors of sulfates into sulfates, stores them, and reduces them to SO₂. Thus, the apparatus little emits the precursors of sulfates to the outside, and can inhibit the particulates emission for a long period of time.

FIG. 1



Description**BACKGROUND OF THE INVENTION****5 Field of the Invention**

The present invention relates to an apparatus for oxidizing and purifying at least hydrocarbons (hereinafter abbreviated to as "HC"), included in an exhaust gas emitted from a diesel engine, and for further inhibiting precursors of sulfates (i.e., SO_3 , SO_4^{2-} , H_2SO_4 , etc.) from being emitted. It is possible for an apparatus according to the present 10 invention to maintain not only the HC oxidizing performance but also the sulfate-precursor emission controlling performance for a long period of time.

Description of the Related Art

15 Concerning gasoline engines, the harmful components included in the exhaust gases emitted therefrom have been reduced steadily, because of severe regulations to control the exhaust gases, and because of the development of technologies to comply with the regulations.

On the other hand, the exhaust gases emitted from diesel engines have been controlled under less stricter regulations than those emitted from gasoline engines, and the technologies for processing the exhaust gases emitted from 20 diesel engines have been developed slower so far than those for the exhaust gases emitted from gasoline engines, because of the special circumstances: namely; diesel engines emit the harmful substances mainly as particulates. Thus, there has been a long-felt need for developing a catalyst which can securely purify the exhaust gases emitted from diesel engines.

As conventional apparatuses developed so far for purifying the exhaust gases emitted from diesel engines, there 25 have been known an apparatus using a trapping element, and an open type oxidizing catalyst. The apparatus using a trapping element can be classified into an apparatus free from a catalyst, and an apparatus provided with a catalyst.

The conventional trapping type apparatus captures the diesel particulates, included in exhaust gases emitted from diesel engines, in order to inhibit them from being emitted to the outside, and is especially effective to the exhaust gases of high dry-soot content. However, the conventional trapping type apparatus requires a recycling apparatus for burning 30 the captured diesel particulates. Accordingly, in view of actual application, there still remain the following problems associated with the conventional trapping type apparatus: namely; its DPF (i.e., diesel particulates filter) is cracked during the recycling operation; its DPF is clogged by ashes; and the conventional trapping type apparatus itself complicates an exhaust system inevitably.

Whilst, one of the open type oxidizing catalysts is disclosed in Japanese Unexamined Patent Publication (KOKAI) 35 No. 1-171,626, for example. As set forth in the publication, similarly to catalysts for purifying exhaust gases emitted from gasoline engines, a catalyst is utilized which comprises a catalyst carrier layer formed of activated alumina, etc., and a catalyst ingredient, such as a platinum-group catalyst ingredient, etc., loaded on the catalyst carrier layer. This open type oxidizing catalyst has a disadvantage in that it removes the dry soot with a low removing rate. However, the quantity of dry soot can be reduced by improving diesel engines or fuels themselves. In addition, engineers have been studying 40 the open type oxidizing catalyst intensively so far, because of a big advantage: namely; no recycling apparatus is required of the open type oxidizing catalyst. Thus, a further engineering improvement is longed for the open type oxidizing catalyst.

Although the open type oxidizing catalyst can efficiently decompose soluble organic fractions (hereinafter abbreviated to "SOF") at elevated temperatures, it suffers from a disadvantage in that its catalyst ingredient exhibits a poor catalytic activity at low temperatures to show deteriorated SOF purifying performance. When an engine is started or operated idly where the temperature of an exhaust gas is low, SOF are not decomposed but turned into soot. Consequently, there arises a phenomenon that the resulting soot deposits in the honeycomb-shaped cellular passages of the catalyst support of the open type oxidizing catalyst. As a result, there arises a disadvantage in that the open type oxidizing catalyst is clogged by the deposited soot to suffer from deteriorated catalytic performance.

50 Moreover, when the open type oxidizing catalyst is improved in terms of the oxidizing performance so that the HC and SOF purifying performance can be enhanced at low temperatures, it suffers from another problem in that the emission of particulates may be enlarged: namely; SO_2 is oxidized to produce SO_3 , SO_4^{2-} , H_2SO_4 , etc., in a high-temperature range, and the resulting SO_3 , SO_4^{2-} , H_2SO_4 , etc., adversely increase the emission of particulates. This drawback results from the fact that the SO_2 is not measured as particulates, but SO_3 , SO_4^{2-} , H_2SO_4 , etc., are measured as particulates. Especially, in the exhaust gases emitted from diesel engines, gaseous oxygen exists in a sufficient amount so that the oxidation of SO_2 is likely to take place.

In order to solve the problems associated with the conventional apparatuses for purifying the exhaust gases emitted from diesel engines, Japanese Unexamined Patent Publication (KOKAI) No. 4-171,215 discloses a novel exhaust

gas purifying apparatus in which an SO₂ trap for capturing SO₂ is disposed on an upstream side with respect to an oxidizing catalyst in an exhaust system. In the novel exhaust gas purifying apparatus, the SO₂ trap includes active alumina, and a base metal. In accordance with the novel exhaust gas purifying apparatus, SO₂, included in an exhaust gas, is reacted with the base metal, and is captured by the SO₂ trap. Consequently, an exhaust gas, being free from the SO₂ component, is supplied to the oxidizing catalyst. As a result, SO₃, SO₄²⁻, H₂SO₄, etc., are inhibited from generating.

However, in the novel exhaust gas purifying apparatus disclosed in Japanese Unexamined Patent Publication (KOKAI) No. 4-171,215, the SO₂ captured by the SO₂ trap accumulates, and the accumulation reaches the saturated state eventually. When the accumulation is saturated, it is difficult for the SO₂ trap to capture SO₂ more than the saturated accumulation. Accordingly, SO₂, not captured by the SO₂ trap, flows to the downstream side, and is oxidized by the oxidizing catalyst to inevitably generate SO₃, SO₄²⁻, H₂SO₄, etc. As a result, it is hard for the novel exhaust gas purifying apparatus to keep the particulate-generation inhibiting function for a long period of time.

SUMMARY OF THE INVENTION

The present invention has been developed in view of the aforementioned circumstances. It is therefore an object of the present to provide an apparatus for purifying an exhaust gas emitted from a diesel engine, apparatus which is good in terms of the HC and SOF purifying performance, and which can inhibit the precursors of sulfates (i.e., SO₃, SO₄²⁻, H₂SO₄, etc.) from being emitted for a long period of time.

An apparatus for purifying an exhaust gas emitted from a diesel engine can carry out the aforementioned object, and comprises:

an oxidizing catalyst disposed on an upstream side in an exhaust system of a diesel engine, and being capable of oxidizing and purifying at least HC included in an exhaust gas emitted from the diesel engine; and
a sulfate-storing-and-reducing catalyst being not only capable of capturing precursors of sulfates, generated at said oxidizing catalyst, as sulfates, but also capable of reducing the captured sulfates to sulfur dioxide (SO₂), and disposed on a downstream side with respect to said oxidizing catalyst in the exhaust system.

In the present exhaust gas purifying apparatus, the exhaust gas emitted from a diesel engine is first brought into contact with the oxidizing catalyst. Accordingly, HC, CO and SOF, included in the exhaust gas, are oxidized by the oxidizing catalyst, and purified to H₂O, CO₂, etc. Moreover, SO₂, included in the exhaust gas, is also oxidized by the oxidizing catalyst to generate the precursors of sulfates (i.e., SO₃, SO₄²⁻, H₂SO₄, etc.).

However, the sulfate-storing-and-reducing catalyst is disposed on a downstream side with respect to the oxidizing catalyst in the exhaust system. The resulting precursors of sulfates (i.e., SO₃, SO₄²⁻, H₂SO₄, etc.) are stored as sulfates on the sulfate-storing-and-reducing catalyst. Thus, SO₃, SO₄²⁻, H₂SO₄, etc., are kept from being emitted to the outside. In addition, the sulfates, which result from SO₃, SO₄²⁻, H₂SO₄, etc., are decomposed by the sulfate-storing-and-reducing catalyst to SO₂ at relatively low temperatures, and the resulting SO₂ is subsequently emitted to the outside. Thus, the sulfates are inhibited from being accumulated on the sulfate-storing-and-reducing catalyst. Hence, the sulfate-storing-and-reducing action of the sulfate-storing-and-reducing catalyst can be kept for a long period of time. As a result, the present exhaust gas purifying apparatus can inhibit SO₃, SO₄²⁻, H₂SO₄, etc., from being emitted to the outside for a long period of time.

As having described so far, the present exhaust gas purifying apparatus can not only oxidize and purify HC, CO and SOF in the same manner as the conventional exhaust gas purifying apparatuses, but also can capture the sulfates, which are derived from SO₃, SO₄²⁻, H₂SO₄, etc., to keep them from being emitted to the outside. In addition, the captured sulfates are reduced to SO₂, and are emitted as SO₂ to the outside. Hence, the sulfate-capturing function of the sulfate-storing-and-reducing catalyst can be recovered. All in all, the sulfate-capturing function of the present exhaust gas purifying apparatus, and the reducing function thereof can be held for a long period of time.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the present invention and many of its advantages will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings and detailed specification, all of which forms a part of the disclosure:

Fig. 1 is a block diagram for schematically illustrating an arrangement of a First Preferred Embodiment of an exhaust gas purifying apparatus according to the present invention; and
Fig. 2 is a block diagram for schematically illustrating an arrangement of a modified version of the preferred embodiments of the present exhaust gas purifying apparatus.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Having generally described the present invention, a further understanding can be obtained by reference to the specific preferred embodiments which are provided herein for the purpose of illustration only and not intended to limit the scope of the appended claims.

In the present exhaust gas purifying apparatus, the oxidizing catalyst oxidizes HC, CO and SOF, included in an exhaust gas emitted from a diesel engine, to convert them into H_2O and CO_2 , thereby purifying the exhaust gas. As the oxidizing catalyst, it is possible to employ the same oxidizing catalysts as the conventional open type oxidizing catalysts. For example, the oxidizing catalyst can be exemplified by one which includes a porous catalyst support, and a catalyst ingredient loaded on the porous catalyst support. The porous catalyst support can be formed of alumina (Al_2O_3), silica (SiO_2), silica-alumina (or a composite oxide of silica and alumina), zirconia (ZrO_2), titania (TiO_2), or zeolite. The catalyst ingredient can be at least one member selected from the group consisting of platinum (Pt), rhodium (Rh), palladium (Pd), ruthenium (Ru), iridium (Ir), etc.

In the oxidizing catalyst, the catalyst ingredient can preferably be loaded on the porous catalyst support in an amount of from 0.1 to 20 grams, further preferably from 1 to 5 grams, with respect to 1 liter of the resulting oxidizing catalyst. When the loading amount is less than 0.1 gram with respect to 1 liter of the resulting oxidizing catalyst, oxidizing activity is little given to the resultant oxidizing catalyst, and accordingly HC, CO and SOF are emitted as they are. When the loading amount is more than 20 grams with respect to 1 liter of the resulting oxidizing catalyst, not only the catalytic action of the resultant oxidizing catalyst is saturated, but also the manufacturing cost thereof is increased.

In the present exhaust gas purifying apparatus, the sulfate-storing-and-reducing catalyst includes a porous catalyst support, and a sulfate-storing-and-reducing ingredient. The thus arranged sulfate-storing-and-reducing catalyst stores the precursors of sulfates (SO_3 , SO_4^{2-} , H_2SO_4 , etc.) which are produced by the oxidizing action of the oxidizing catalyst, as sulfates on the sulfate-storing-and-reducing ingredient. The stored sulfates are then decomposed to SO_2 at relatively low temperatures, and are emitted to recover the sulfate-storing-and-reducing ingredient. Consequently, the present exhaust gas purifying apparatus can effectively inhibit SO_3 , SO_4^{2-} , H_2SO_4 , etc., from being emitted to the outside, and can simultaneously keep the sulfate-storing-and-reducing activity for a long period of time.

As for the sulfate-storing-and-reducing ingredient, it is possible to employ at least one member selected from the group consisting of alkali metal elements, alkaline-earth metal elements, and transition elements. Among the transition elements, it is preferred to select at least one member from the group consisting of iron (Fe), copper (Cu), molybdenum (Mo), and tungsten (W), because these elements react with the precursors of sulfates (i.e., SO_3 , SO_4^{2-} , H_2SO_4 , etc.) to produce the sulfates which can be decomposed in a low temperature range, for instance, 500 °C or less. Thus, these transition elements can be especially effective for processing an exhaust gas of low temperatures emitted from a diesel engine. It is further preferred that the resulting sulfates be decomposed in a low temperature range of from 300 to 500 °C. When the exhaust gas is heated to above 500 °C, the sulfate-storing-and-reducing ingredient can not only be the aforementioned transition elements but also sodium (Na), barium (Ba) or cobalt (Co) whose sulfates are less likely to decompose at 500 °C or less. Note that the sulfate-storing-and-reducing ingredient can preferably be loaded on a porous catalyst support which is formed of alumina (Al_2O_3), titania (TiO_2), a mixture of alumina and silica (SiO_2), a mixture of alumina and zirconia (ZrO_2), a mixture of titania and silica, or a mixture of titania and zirconia.

The alumina and titania are especially preferred as the porous support of the sulfate-storing-and-reducing catalyst, because they have acidic sites so that the sulfates are likely to be decomposed. Whilst, the silica and zirconia are not so preferable as the alumina and titania, because they are so acidic that they are less likely to adsorb SO_3 , SO_4^{2-} , H_2SO_4 , etc., thereon. However, when the silica and zirconia are mixed with the alumina and titania, they can be used also as the porous support of the sulfate-storing-and-reducing catalyst.

In the sulfate-storing-and-reducing catalyst, the sulfate-storing-and-reducing ingredient can preferably be loaded on the porous catalyst support in an amount of from 0.05 to 2 moles, further preferably from 0.1 to 0.5 moles, with respect to 1 liter of the resulting sulfate-storing-and-reducing catalyst. When the loading amount is less than 0.05 moles with respect to 1 liter of the resulting sulfate-storing-and-reducing catalyst, the sulfates, derived from SO_3 , SO_4^{2-} , H_2SO_4 , etc., are reduced in a lesser amount. Accordingly, the adsorption of the sulfates is readily saturated, and subsequently the emission of SO_3 , SO_4^{2-} , H_2SO_4 , etc., is increased. When the loading amount is more than 2 moles with respect to 1 liter of the resulting sulfate-storing-and-reducing catalyst, the reducing activity of the resultant sulfate-storing-and-reducing catalyst is saturated so that the sulfate-storing-and-reducing ingredient is loaded uselessly.

The actions of the thus arranged sulfate-storing-and-reducing catalyst will be hereinafter described in detail. For example, when the sulfate-storing-and-reducing catalyst includes a catalyst support formed of alumina, and iron oxides loaded on the catalyst support, the precursors of sulfates (i.e., SO_3 , SO_4^{2-} , H_2SO_4 , etc.) are believed to be adsorbed onto the alumina, and to be reacted with the iron oxides to turn into iron sulfates. Then, the resulting iron sulfates are decomposed to SO_2 in a low temperature range, for instance, 500 °C or less, and are thereafter emitted as SO_2 to the outside. As a result, the present exhaust gas purifying apparatus can inhibit SO_3 , SO_4^{2-} , H_2SO_4 , etc., from being emitted to the outside.

After the oxidizing catalyst and the sulfate-storing-and-reducing catalyst are prepared as described above, they can be arranged positionally so that they are disposed in the following manner: the oxidizing catalyst is disposed on an upstream side in an exhaust system of a diesel engine, for example, adjacent to a diesel engine as close as possible (or immediately below an exhaust manifold of a diesel engine); and the sulfate-storing-and-reducing catalyst is disposed on a downstream side with respect to the oxidizing catalyst in the exhaust system. In this instance, the interval between the oxidizing catalyst and the sulfate-storing-and-reducing catalyst is not specified in particular. For instance, the oxidizing catalyst and the sulfate-storing-and-reducing catalyst can be disposed adjacent to each other, they can be contacted with each other, or they can be disposed away from each other with a predetermined interval provided therebetween. Note that, however, the temperature of the exhaust gas is decreased as it is measured on a further downstream side in the exhaust system. Hence, the sulfate-storing-and-reducing catalyst can preferably be positioned within a downstream area where the temperature of the exhaust gas is held in such a range that the sulfate-storing-and-reducing catalyst can effect its catalytic action most efficiently.

Alternatively, the present exhaust gas purifying apparatus can be constructed as an integral unit: namely; an oxidizing catalyst can be formed on a unitary honeycomb-shaped support substrate on an upstream side thereof in the direction of an exhaust gas flow; and a sulfate-storing-and-reducing catalyst can be formed on the unitary honeycomb-shaped support substrate on a downstream side with respect to the oxidizing catalyst.

The present catalytic apparatus will be hereinafter described in detail with reference to preferred embodiments and comparative examples.

20 First Preferred Embodiment

(Preparation of Sulfate-Storing-and-Reducing Catalyst)

A predetermined amount of an alumina powder was added into a prescribed amount of an aqueous solution of iron nitrate having a specific concentration. The resulting mixture was stirred at room temperature for 1 hour. Thereafter, the mixture was dried at 100 °C for 5 hours, and was subsequently calcinated at 650 °C for 1 hour to prepare an alumina-iron powder (i.e., an alumina powder with iron oxides loaded).

The thus prepared alumina-iron powder was added to distilled water along with an alumina sol, thereby preparing a slurry. Note that the alumina sol contained alumina in an amount of 5% by weight. Then, a honeycomb-shaped support substrate was immersed into the resulting slurry. The honeycomb-shaped support substrate had a volume of 1.7 L, and was formed of cordierite. Thereafter, the honeycomb-shaped support substrate was taken out of the slurry, and was blown off to remove excessive slurry. Finally, the honeycomb-shaped support substrate was dried at 120 °C for 10 hours, and was subsequently calcinated at 700 °C for 2 hours. Thus, a coating layer was formed on the honeycomb-shaped support substrate, thereby completing a sulfate-storing-and-reducing catalyst.

The thus prepared sulfate-storing-and-reducing catalyst included an alumina coating layer, and iron oxides loaded on the alumina coating layer. The alumina coating layer was formed in an amount of 120 grams with respect to 1 L of the honeycomb-shaped support substrate. The iron oxides were loaded on the alumina coating layer in an amount of 0.3 moles with respect to 1 L of the honeycomb-shaped support substrate. Note that the loading amount of the iron oxides was converted into an amount of metallic iron.

40

(Preparation of Oxidizing Catalyst)

Another alumina powder was added to distilled water along with another alumina sol, thereby preparing another slurry. Note that the alumina sol contained alumina in an amount of 5% by weight. Then, another honeycomb-shaped support substrate was immersed into the resulting slurry. Likewise, the honeycomb-shaped support substrate had a volume of 1.7 L, and was formed of cordierite. Thereafter, the honeycomb-shaped support substrate was taken out of the slurry, and was blown off to remove excessive slurry. Then, the honeycomb-shaped support substrate was dried at 120 °C for 10 hours, and was subsequently calcinated at 500 °C for 2 hours. Thus, a coating layer was formed on the honeycomb-shaped support substrate.

50

Whilst, an aqueous solution of dinitrodiammine platinum nitrate was prepared to have a predetermined concentration. The honeycomb-shaped support substrate with the aforementioned alumina coating layer formed thereon was immersed into the aqueous solution. Thereafter, the honeycomb-shaped support substrate was taken out of the aqueous solution, and was blown off to remove excessive water droplets. Then, the honeycomb-shaped support substrate was dried at 120 °C for 10 hours, and was subsequently calcinated at 250 °C for 1 hour. Thus, an oxidizing catalyst was completed.

The thus prepared oxidizing catalyst included an alumina coating layer, and metallic platinum loaded on the alumina coating layer. The alumina coating layer was formed in an amount of 120 grams with respect to 1 L of the honeycomb-shaped support substrate. The metallic platinum was loaded on the alumina coating layer in an amount of 1 gram

with respect to 1 L of the honeycomb-shaped support substrate.

(Arrangement of Exhaust Gas Purifying Apparatus)

5 Then, as illustrated in Fig. 1, the resultant oxidizing catalyst was disposed on an upstream side in an exhaust system 30 of a diesel engine 3, and the resultant sulfate-storing-and-reducing catalyst was disposed on a downstream side with respect to the oxidizing catalyst in the exhaust system 30. In the drawing, the oxidizing catalyst is designated at 1, and the sulfate-storing-and-reducing catalyst is designated at 2. The diesel engine 3 had a displacement of 2.4 L.

10 **(Examination and Evaluation)**

The diesel engine 3 was operated in a temperature range of from 200 to 500 °C under the ordinary rated conditions. Note that the operating temperature was increased by 50 °C for every 1 minute. The exhaust gas was examined for an SO₂ concentration (C₁) at the outlet of the oxidizing catalyst, and was further examined for an SO₂ concentration (C₂) 15 at the outlet of the sulfate-storing-and-reducing catalyst. A sulfate reducing rate was calculated by the following equation:

$$\text{Sulfate Reducing Rate (\%)} = \{(C_2 - C_1)/C_1\} \times 100.$$

20 The result of the examination is summarized in Table 1 below.

Second Preferred Embodiment

Instead of the aqueous solution of iron nitrate, an aqueous solution of copper nitrate having a specific concentration 25 was used to prepare a sulfate-storing-and-reducing catalyst of a Second Preferred Embodiment. Unless otherwise specified, the sulfate-storing-and-reducing catalyst of the Second Preferred Embodiment was completed in the same manner as that of the First Preferred Embodiment. The resultant sulfate-storing-and-reducing catalyst included an alumina coating layer, and copper oxides loaded on the alumina coating layer. The alumina coating layer was formed in an amount of 120 grams with respect to 1 L of the honeycomb-shaped support substrate. The copper oxides were loaded 30 on the alumina coating layer in an amount of 0.3 moles with respect to 1 L of the honeycomb-shaped support substrate. Note that the loading amount of the copper oxides was converted into an amount of metallic copper.

Whilst, an oxidizing catalyst of the Second Preferred Embodiment was prepared in the identical manner with that of the First Preferred Embodiment. Then, the oxidizing catalyst as well as the sulfate-storing-and-reducing catalyst were disposed to construct an exhaust gas purifying apparatus in the same fashion as that of the First Preferred Embodiment. The resultant exhaust gas purifying apparatus was examined for the sulfate reducing rate under the aforementioned conditions. The result of the examination is also summarized in Table 1 below.

Third Preferred Embodiment

40 Instead of the aqueous solution of iron nitrate, an aqueous solution of ammonium molybdate having a specific concentration was used to prepare a sulfate-storing-and-reducing catalyst of a Third Preferred Embodiment. Unless otherwise specified, the sulfate-storing-and-reducing catalyst of the Third Preferred Embodiment was completed in the same manner as that of the First Preferred Embodiment. The resultant sulfate-storing-and-reducing catalyst included an alumina coating layer, and molybdenum oxides loaded on the alumina coating layer. The alumina coating layer was formed 45 in an amount of 120 grams with respect to 1 L of the honeycomb-shaped support substrate. The molybdenum oxides were loaded on the alumina coating layer in an amount of 0.3 moles with respect to 1 L of the honeycomb-shaped support substrate. Note that the loading amount of the molybdenum oxides was converted into an amount of metallic molybdenum.

Whilst, an oxidizing catalyst of the Third Preferred Embodiment was prepared in the identical manner with that of the First Preferred Embodiment. Then, the oxidizing catalyst as well as the sulfate-storing-and-reducing catalyst were disposed to construct an exhaust gas purifying apparatus in the same fashion as that of the First Preferred Embodiment. The resultant exhaust gas purifying apparatus was examined for the sulfate reducing rate under the aforementioned conditions. The result of the examination is also summarized in Table 1 below.

55 **Fourth Preferred Embodiment**

Instead of the aqueous solution of iron nitrate, an aqueous solution of ammonium tungstate having a specific concentration was used to prepare a sulfate-storing-and-reducing catalyst of a Fourth Preferred Embodiment. Unless oth-

erwise specified, the sulfate-storing-and-reducing catalyst of the Fourth Preferred Embodiment was completed in the same manner as that of the First Preferred Embodiment. The resultant sulfate-storing-and-reducing catalyst included an alumina coating layer, and tungsten oxides loaded on the alumina coating layer. The alumina coating layer was formed in an amount of 120 grams with respect to 1 L of the honeycomb-shaped support substrate. The tungsten oxides were loaded on the alumina coating layer in an amount of 0.3 moles with respect to 1 L of the honeycomb-shaped support substrate. Note that the loading amount of the tungsten oxides was converted into an amount of metallic tungsten.

Whilst, an oxidizing catalyst of the Fourth Preferred Embodiment was prepared in the identical manner with that of the First Preferred Embodiment. Then, the oxidizing catalyst as well as the sulfate-storing-and-reducing catalyst were disposed to construct an exhaust gas purifying apparatus in the same fashion as that of the First Preferred Embodiment. The resultant exhaust gas purifying apparatus was examined for the sulfate reducing rate under the aforementioned conditions. The result of the examination is also summarized in Table 1 below.

Fifth Preferred Embodiment

Instead of the alumina powder, a titania powder was used for the preparation of a sulfate-storing-and-reducing catalyst of a Fifth Preferred Embodiment. Instead of the alumina sol, a titania sol was used therefor. Unless otherwise specified, the sulfate-storing-and-reducing catalyst of the Fifth Preferred Embodiment was completed in the same manner as that of the First Preferred Embodiment. The resultant sulfate-storing-and-reducing catalyst included a titania coating layer, and iron oxides loaded on the titania coating layer. The titania coating layer was formed in an amount of 120 grams with respect to 1 L of the honeycomb-shaped support substrate. The iron oxides were loaded on the titania coating layer in an amount of 0.3 moles with respect to 1 L of the honeycomb-shaped support substrate. Note that the loading amount of the iron oxides was converted into an amount of metallic iron.

Whilst, an oxidizing catalyst of the Fifth Preferred Embodiment was prepared in the identical manner with that of the First Preferred Embodiment. Then, the oxidizing catalyst as well as the sulfate-storing-and-reducing catalyst were disposed to construct an exhaust gas purifying apparatus in the same fashion as that of the First Preferred Embodiment. The resultant exhaust gas purifying apparatus was examined for the sulfate reducing rate under the aforementioned conditions. The result of the examination is also summarized in Table 1 below.

Sixth Preferred Embodiment

Instead of the alumina powder, a titania powder was used for the preparation of a sulfate-storing-and-reducing catalyst of a Sixth Preferred Embodiment. Instead of the alumina sol, a titania sol was used therefor. Instead of the aqueous solution of iron nitrate, an aqueous solution of copper nitrate having a specific concentration was used therefor. Unless otherwise specified, the sulfate-storing-and-reducing catalyst of the Sixth Preferred Embodiment was completed in the same manner as that of the First Preferred Embodiment. The resultant sulfate-storing-and-reducing catalyst included a titania coating layer, and copper oxides loaded on the titania coating layer. The titania coating layer was formed in an amount of 120 grams with respect to 1 L of the honeycomb-shaped support substrate. The copper oxides were loaded on the titania coating layer in an amount of 0.3 moles with respect to 1 L of the honeycomb-shaped support substrate. Note that the loading amount of the copper oxides was converted into an amount of metallic copper.

Whilst, an oxidizing catalyst of the Sixth Preferred Embodiment was prepared in the identical manner with that of the First Preferred Embodiment. Then, the oxidizing catalyst as well as the sulfate-storing-and-reducing catalyst were disposed to construct an exhaust gas purifying apparatus in the same fashion as that of the First Preferred Embodiment. The resultant exhaust gas purifying apparatus was examined for the sulfate reducing rate under the aforementioned conditions. The result of the examination is also summarized in Table 1 below.

Seventh Preferred Embodiment

Instead of the alumina powder, a titania powder was used for the preparation of a sulfate-storing-and-reducing catalyst of a Seventh Preferred Embodiment. Instead of the alumina sol, a titania sol was used therefor. Instead of the aqueous solution of iron nitrate, an aqueous solution of ammonium molybdate having a specific concentration was used therefor. Unless otherwise specified, the sulfate-storing-and-reducing catalyst of the Seventh Preferred Embodiment was completed in the same manner as that of the First Preferred Embodiment. The resultant sulfate-storing-and-reducing catalyst included a titania coating layer, and molybdenum oxides loaded on the titania coating layer. The titania coating layer was formed in an amount of 120 grams with respect to 1 L of the honeycomb-shaped support substrate. The molybdenum oxides were loaded on the titania coating layer in an amount of 0.3 moles with respect to 1 L of the honeycomb-shaped support substrate. Note that the loading amount of the molybdenum oxides was converted into an amount of metallic molybdenum.

Whilst, an oxidizing catalyst of the Seventh Preferred Embodiment was prepared in the identical manner with that

of the First Preferred Embodiment. Then, the oxidizing catalyst as well as the sulfate-storing-and-reducing catalyst were disposed to construct an exhaust gas purifying apparatus in the same fashion as that of the First Preferred Embodiment. The resultant exhaust gas purifying apparatus was examined for the sulfate reducing rate under the aforementioned conditions. The result of the examination is also summarized in Table 1 below.

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Eighth Preferred Embodiment

Instead of the alumina powder, a titania powder was used for the preparation of a sulfate-storing-and-reducing catalyst of an Eighth Preferred Embodiment. Instead of the alumina sol, a titania sol was used therefor. Instead of the aqueous solution of iron nitrate, an aqueous solution of ammonium tungstate having a specific concentration was used therefor. Unless otherwise specified, the sulfate-storing-and-reducing catalyst of the Eighth Preferred Embodiment was completed in the same manner as that of the First Preferred Embodiment. The resultant sulfate-storing-and-reducing catalyst included a titania coating layer, and tungsten oxides loaded on the titania coating layer. The titania coating layer was formed in an amount of 120 grams with respect to 1 L of the honeycomb-shaped support substrate. The tungsten oxides were loaded on the titania coating layer in an amount of 0.3 moles with respect to 1 L of the honeycomb-shaped support substrate. Note that the loading amount of the tungsten oxides was converted into an amount of metallic tungsten.

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Whilst, an oxidizing catalyst of the Eighth Preferred Embodiment was prepared in the identical manner with that of the First Preferred Embodiment. Then, the oxidizing catalyst as well as the sulfate-storing-and-reducing catalyst were disposed to construct an exhaust gas purifying apparatus in the same fashion as that of the First Preferred Embodiment. The resultant exhaust gas purifying apparatus was examined for the sulfate reducing rate under the aforementioned conditions. The result of the examination is also summarized in Table 1 below.

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Comparative Example Nos. 1 through 4

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Instead of the alumina powder, a silica powder was used for the preparation of a sulfate-storing-and-reducing catalyst of Comparative Example Nos. 1 through 4. Instead of the alumina sol, a silica sol was used therefor. Unless otherwise specified, the sulfate-storing-and-reducing catalyst of Comparative Example Nos. 1 through 4 was completed in the same manner as those of the First through Fourth Preferred Embodiments, respectively.

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Whilst, an oxidizing catalyst of Comparative Example Nos. 1 through 4 was prepared in the identical manner with that of the First Preferred Embodiment. Then, the oxidizing catalyst as well as the sulfate-storing-and-reducing catalyst were disposed to construct an exhaust gas purifying apparatus in the same fashion as that of the First Preferred Embodiment. The resultant exhaust gas purifying apparatuses were examined for the sulfate reducing rate under the aforementioned conditions. The results of the examinations are also summarized in Table 1 below.

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Comparative Example Nos. 5 through 8

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Instead of the alumina powder, a zirconia powder was used for the preparation of a sulfate-storing-and-reducing catalyst of Comparative Example Nos. 5 through 8. Instead of the alumina sol, a zirconia sol was used therefor. Unless otherwise specified, the sulfate-storing-and-reducing catalyst of Comparative Example Nos. 5 through 8 was completed in the same manner as those of the Fifth through Eighth Preferred Embodiments, respectively.

Whilst, an oxidizing catalyst of Comparative Example Nos. 5 through 8 was prepared in the identical manner with that of the First Preferred Embodiment. Then, the oxidizing catalyst as well as the sulfate-storing-and-reducing catalyst was disposed to construct an exhaust gas purifying apparatus in the same fashion as that of the First Preferred Embodiment. The resultant exhaust gas purifying apparatuses were examined for the sulfate reducing rate under the aforementioned conditions. The results of the examinations are also summarized in Table 1 below.

Comparative Example No. 9

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Instead of the aqueous solution of iron nitrate, an aqueous solution of cobalt nitrate having a specific concentration was used to prepare a sulfate-storing-and-reducing catalyst of Comparative Example No. 9. Unless otherwise specified, the sulfate-storing-and-reducing catalyst of Comparative Example No. 9 was completed in the same manner as that of the First Preferred Embodiment. The resultant sulfate-storing-and-reducing catalyst included an alumina coating layer, and cobalt oxides loaded on the alumina coating layer. The alumina coating layer was formed in an amount of 120 grams with respect to 1 L of the honeycomb-shaped support substrate. The cobalt oxides were loaded on the alumina coating layer in an amount of 0.3 moles with respect to 1 L of the honeycomb-shaped support substrate. Note that the loading amount of the cobalt oxides was converted into an amount of metallic cobalt.

Whilst, an oxidizing catalyst of Comparative Example No. 9 was prepared in the identical manner with that of the

First Preferred Embodiment. Then, the oxidizing catalyst as well as the sulfate-storing-and-reducing catalyst were disposed to construct an exhaust gas purifying apparatus in the same fashion as that of the First Preferred Embodiment. The resultant exhaust gas purifying apparatus was examined for the sulfate reducing rate under the aforementioned conditions. The result of the examination is also summarized in Table 2 below.

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Comparative Example No. 10

Instead of the aqueous solution of iron nitrate, an aqueous solution of barium acetate having a specific concentration was used to prepare a sulfate-storing-and-reducing catalyst of Comparative Example No. 10. Unless otherwise specified, the sulfate-storing-and-reducing catalyst of Comparative Example No. 10 was completed in the same manner as that of the First Preferred Embodiment. The resultant sulfate-storing-and-reducing catalyst included an alumina coating layer, and barium oxides loaded on the alumina coating layer. The alumina coating layer was formed in an amount of 120 grams with respect to 1 L of the honeycomb-shaped support substrate. The barium oxides were loaded on the alumina coating layer in an amount of 0.3 moles with respect to 1 L of the honeycomb-shaped support substrate.

15 Note that the loading amount of the barium oxides was converted into an amount of metallic barium.

Whilst, an oxidizing catalyst of Comparative Example No. 10 was prepared in the identical manner with that of the First Preferred Embodiment. Then, the oxidizing catalyst as well as the sulfate-storing-and-reducing catalyst were disposed to construct an exhaust gas purifying apparatus in the same fashion as that of the First Preferred Embodiment. The resultant exhaust gas purifying apparatus was examined for the sulfate reducing rate under the aforementioned 20 conditions. The result of the examination is also summarized in Table 2 below.

Comparative Example No. 11

Instead of the aqueous solution of iron nitrate, an aqueous solution of sodium nitrate having a specific concentration was used to prepare a sulfate-storing-and-reducing catalyst of Comparative Example No. 11. Unless otherwise specified, the sulfate-storing-and-reducing catalyst of Comparative Example No. 11 was completed in the same manner as that of the First Preferred Embodiment. The resultant sulfate-storing-and-reducing catalyst included an alumina coating layer, and sodium oxides loaded on the alumina coating layer. The alumina coating layer was formed in an amount of 120 grams with respect to 1 L of the honeycomb-shaped support substrate. The sodium oxides were loaded 30 on the alumina coating layer in an amount of 0.3 moles with respect to 1 L of the honeycomb-shaped support substrate. Note that the loading amount of the sodium oxides was converted into an amount of metallic sodium.

Whilst, an oxidizing catalyst of Comparative Example No. 11 was prepared in the identical manner with that of the First Preferred Embodiment. Then, the oxidizing catalyst as well as the sulfate-storing-and-reducing catalyst were disposed to construct an exhaust gas purifying apparatus in the same fashion as that of the First Preferred Embodiment. 35 The resultant exhaust gas purifying apparatus was examined for the sulfate reducing rate under the aforementioned conditions. The result of the examination is also summarized in Table 2 below.

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TABLE 1

Identification	Sulfate-Storing-and-Reducing Catalyst		Sulfate Reducing Rate (%)
	Loaded Catalyst Ingredient (Loading Amount)	Coating Layer	
1st Pref. Embodiment	Fe (0.3 mole/L)	Al ₂ O ₃	5
2nd Pref Embodiment	Cu (0.3 mole/L)	Al ₂ O ₃	10
3rd Pref. Embodiment	Mo (0.3 mole/L)	Al ₂ O ₃	15
4th Pref. Embodiment	W (0.3 mole/L)	Al ₂ O ₃	10
5th Pref. Embodiment	Fe (0.3 mole/L)	TiO ₂	40
6th Pref. Embodiment	Cu (0.3 mole/L)	TiO ₂	20
7th Pref. Embodiment	Mo (0.3 mole/L)	TiO ₂	10
8th Pref. Embodiment	W (0.3 mole/L)	TiO ₂	5
Comparative Ex. No. 1	Fe (0.3 mole/L)	SiO ₂	0
Comparative Ex. No. 2	Cu (0.3 mole/L)	SiO ₂	0
Comparative Ex. No. 3	Mo (0.3 mole/L)	SiO ₂	0
Comparative Ex. No. 4	W (0.3 mole/L)	SiO ₂	0
Comparative Ex. No. 5	Fe (0.3 mole/L)	ZrO ₂	0
Comparative Ex. No. 6	Cu (0.3 mole/L)	ZrO ₂	0
Comparative Ex. No. 7	Mo (0.3 mole/L)	ZrO ₂	0
Comparative Ex. No. 8	W (0.3 mole/L)	ZrO ₂	0

TABLE 2

Identification	Sulfate-Storing-and-Reducing Catalyst		Sulfate Reducing Rate (%)
	Loaded Catalyst Ingredient (Loading Amount)	Coating Layer	
Comparative Ex. No. 9	Co (0.3 mole/L)	Al ₂ O ₃	0
Comparative Ex. No. 10	Ba (0.3 mole/L)	Al ₂ O ₃	0
Comparative Ex. No. 11	Na (0.3 mole/L)	Al ₂ O ₃	0

It is apparent from Table 1 that the exhaust gas purifying apparatuses of the First through Eighth Preferred Embodiments could efficiently reduce the sulfates. These advantages are believed to result from the action of the acidic sites of the alumina and titania; namely; the acidic sites of the coating layer facilitatively decomposed sulfates which were stored on the sulfate-storing-and-reducing catalysts.

On the other hand, the exhaust gas purifying apparatuses of Comparative Example Nos. 1 through 8 seem to have little adsorbed the precursors of sulfates (i.e., SO₃, SO₄²⁻, H₂SO₄, etc.) and to have emitted them as they were, because the coating layers were formed of silica and zirconia which were acidic oxides.

Note that the exhaust gas purifying apparatuses of Comparative Example Nos. 9 through 11 did not reduce the sulfates despite the coating layers which were formed of alumina. This phenomenon results from the fact that the sulfates of Co, Ba and Na have a high decomposition temperature, and that they cannot be decomposed at about 500 °C which

an exhaust gas, emitted from a diesel engine, can exhibit at the highest. Accordingly, by employing a heater for heating the sulfate-storing-and-reducing catalysts, or by employing a heater for heating the exhaust gas being introduced into the sulfate-storing-and-reducing catalysts, the exhaust gas purifying apparatuses of Comparative Example Nos. 9 through 11 can be made to reduce the sulfates in the same way as the First through Eighth Preferred Embodiments.

5 In the First through Eighth Preferred Embodiments, the oxidizing catalysts and the sulfate-storing-and-reducing catalysts were disposed so as to construct a tandem exhaust gas purifying apparatus. Namely, the oxidizing catalysts and the sulfate-storing-and-reducing catalysts were disposed in series with a predetermined interval provided therebetween. Whilst, as illustrated in Fig. 2, an oxidizing catalyst can be formed on a unitary catalyst support on an upstream side thereof in the direction of an exhaust gas flow, and a sulfate-storing-and-reducing catalyst can be formed on the
 10 unitary catalyst support on a downstream side with respect to the oxidizing catalyst. The thus modified exhaust gas purifying catalyst can apparently operate and produce advantages in the same manner as the First through Eighth Preferred Embodiments.

Having now fully described the present invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the present invention as
 15 set forth herein including the appended claims.

An apparatus for purifying an exhaust gas emitted from a diesel engine includes an oxidizing catalyst, and a sulfate-storing-and-reducing catalyst. The oxidizing catalyst is disposed on an upstream side in an exhaust system of a diesel engine, and can oxidize at least HC (i.e., hydrocarbons) contained in an exhaust gas emitted from the diesel engine. The sulfate-storing-and-reducing catalyst can not only capture precursors of sulfates (i.e., SO_3 , SO_4^{2-} , H_2SO_4 , etc.),
 20 generated at the oxidizing catalyst, as sulfates, but also can reduce the captured sulfates to SO_2 , and is disposed on a downstream side with respect to the oxidizing catalyst in the exhaust system. The sulfate-storing-and-reducing catalyst turns the precursors of sulfates into sulfates, stores them, and reduces them to SO_2 . Thus, the apparatus little emits the precursors of sulfates to the outside, and can inhibit the particulates emission for a long period of time.

25 **Claims**

1. An apparatus for purifying an exhaust gas emitted from a diesel engine, comprising:

30 an oxidizing catalyst disposed on an upstream side in an exhaust system of a diesel engine, and being capable of oxidizing and purifying at least HC (i.e., hydrocarbons) included in an exhaust gas emitted from the diesel engine; and
 a sulfate-storing-and-reducing catalyst being not only capable of capturing precursors of sulfates, generated at said oxidizing catalyst, as sulfates, but also capable of reducing the captured sulfates to sulfur dioxide (SO_2), and disposed on a downstream side with respect to said oxidizing catalyst in the exhaust system.

35 2. The apparatus according to Claim 1, wherein said oxidizing catalyst includes a porous catalyst support formed of at least one member which is selected from the group consisting of alumina (Al_2O_3), silica (SiO_2), a composite oxide of silica and alumina, zirconia (ZrO_2), titania (TiO_2), and zeolite, and at least one catalyst ingredient which is selected from the group consisting of platinum (Pt), rhodium (Rh), palladium (Pd), ruthenium (Ru), and iridium (Ir), and which is loaded on the porous catalyst support.

40 3. The apparatus according to Claim 2, wherein said catalyst ingredient is loaded on said porous catalyst support in an amount of from 0.1 to 20 grams with respect to 1 liter of said oxidizing catalyst.

45 4. The apparatus according to Claim 1, wherein said sulfate-storing-and-reducing catalyst includes a porous catalyst support formed of at least one member which is selected from the group consisting of alumina (Al_2O_3), titania (TiO_2), a mixture of alumina and silica (SiO_2), a mixture of alumina and zirconia, a mixture of titania and silica, and a mixture of titania and zirconia, and at least one sulfate-storing-and-reducing ingredient which is selected from the group consisting of alkali metal elements, alkaline-earth metal elements, and transition elements.

50 5. The apparatus according to Claim 4, wherein said sulfate-storing-and-reducing ingredient is at least one member which is selected from the group consisting of transition elements.

55 6. The apparatus according to Claim 5, wherein said sulfate-storing-and-reducing ingredient is at least one member which is selected from the group consisting of iron (Fe), copper (Cu), molybdenum (Mo), and tungsten (W).

7. The apparatus according to Claim 4, wherein said sulfate-storing-and-reducing ingredient is loaded on said porous catalyst support in an amount of from 0.05 to 2 moles with respect to 1 liter of said sulfate-storing-and-reducing cat-

alyst.

8. The apparatus according to Claim 1, wherein said sulfate-storing-and-reducing catalyst turns the precursors of sulfates into sulfates which can be decomposed at a temperature of 500 °C or less.
- 5 9. The apparatus according to Claim 1, wherein said oxidizing catalyst is disposed immediately below an exhaust manifold of a diesel engine, and said sulfate-storing-and-reducing catalyst is disposed within a downstream area where the temperature of the exhaust gas is held in such a range that said sulfate-storing-and-reducing catalyst can effect its catalytic action.
- 10 10. The apparatus according to Claim 1, wherein said oxidizing catalyst is formed on a unitary support substrate on an upstream side thereof in the direction of an exhaust gas flow; and said sulfate-storing-and-reducing catalyst is formed on the unitary support substrate on a downstream side thereof with respect to said oxidizing catalyst.

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FIG. 1

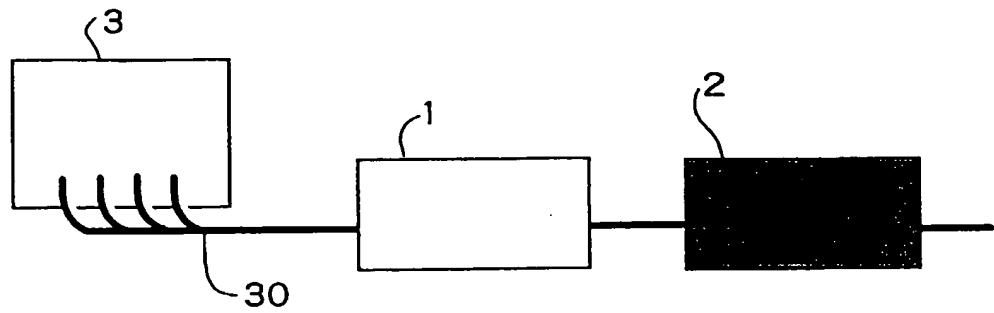
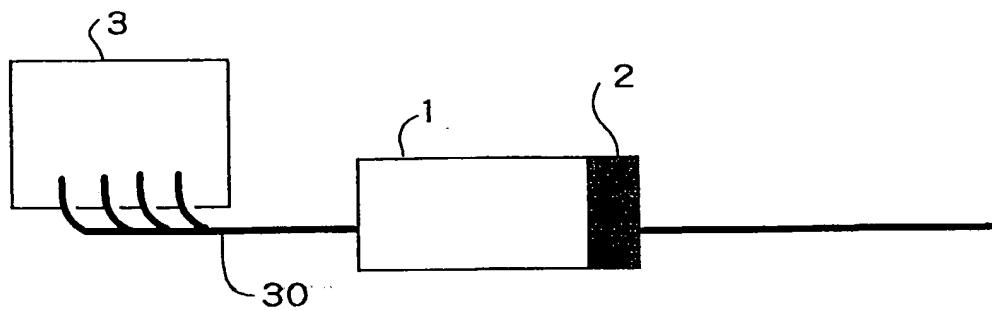


FIG. 2





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 11 1220

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CI.6)
P,X	<p>DATABASE WPI Section Ch, Week 9715 Derwent Publications Ltd., London, GB; Class H06, AN 97-162790 XP002043026 & JP 09 032 539 A (CATALER IND CO LTD) , 4 February 1997 * abstract *</p> <p>---</p>	1	B01D53/94 F01N3/08
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<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	9 October 1997	Sideris, M	
CATEGORY OF CITED DOCUMENTS		<p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>	
<p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p>			



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 613 714 A (TOYOTA MOTOR CO LTD :TOYODA CHUO KENKYUSHO KK (JP); CATALER IND CO) 7 September 1994 * page 5, line 42 - line 44 * * page 5, line 53 - line 57 * * page 6, line 8 - line 12 * * page 6, line 24 - line 31 * -----	1,2,4-6	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims.			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	9 October 1997	Sideris, M	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			